Novel Fluoride-Phosphate Based Cathode Materials for Metal-Ion Batteries

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The metal-ion battery performance critically depends on the properties of a cathode material. Fluoride-phosphate based cathode materials have captured significant attention due to several advantages compared to conventional oxide materials: the increase of the operating potential due to a higher electronegativity of fluorine, better kinetics arising from a lower affinity of alkali ion to the fluoride anion and a wider structural diversity enabled tuning the electrochemical properties.

In our research group a novel series of $KTiOPO_4$ (KTP) type $AVPO_4F$ (A = Li, Na, K, Rb) [1-3] fluoride-phosphate cathode materials was designed and synthesized using hydrothermal and freeze-drying techniques. The peculiarities of the KTP-type "VPO_4F" framework enabled excellent rate capability particularly demonstrated in Li cells [1]. The material showed outstanding capacity retention maintaining more than 75% of the initial specific capacity in Li-ion cells at 40C and an average potential of 4.0 V vs Li/Li^+ with maximal theoretical energy density of more than 650 mWh/g.

The materials also support reversible intercalation of Na^+, K^+ and even Rb^+ ions preserving the host structure. Electrochemical behaviour and ion transport properties were found quite different for Li^+, Na^+, K^+ and Rb^+ ions. The alkali ion diffusion coefficients measured by PITT were the lowest for Li^+ (10^{-12} – 10^{-14} cm^2/s) and highest for K^+ (10^{-11} – 10^{-12} cm^2/s) [2]. The energy barriers of K^+ and Rb^+ migration calculated using the DFT-NEB methodology are found to be exceptionally low not exceeding 0.2 eV and correlating well with the experimentally determined diffusion coefficients. These results suggest a new paradigm for designing new polyanion-based cathodes for alternative metal-ion batteries with unique electrochemical properties.

In this report we will focus on our recent activities on the KTP-type fluoride-phosphates considered as promising cathode materials for metal-ion rechargeable batteries.

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[2] V.A. Nikitina et al. *J. Electrochem. Soc*. **164** (2017) A6373
[3] V. A. Nikitina et al. *Electrochim. Acta.* **258** (2017) 814